needles) should be employed. Only all-glass reaction vessels, gas-tight syringes with Teflon luer-lock hubs, and Teflon syringe needles and cannulas were used. Peroxytrifluoroacetic acid was prepared only as needed according to a modification of a literature procedure,[13] where 30% H_2O_2 was substituted for 90% H_2O_2 and, for some cases, trifluoroacetic acid[19] was substituted for dichloromethane as solvent. Benzene (thiophene free) was distilled from sodium/benzophenone under argon before use. Cobalt(II) acetate, trifluoroacetic acid, trifluoroacetic anhydride, acetaldehyde, 35% peracetic acid, and 30% H_2O_2 were obtained from commercial sources and used as received; a sample of 70% H_2O_2 (Albone 70) was obtained from DuPont. Benzene[20] and trifluoroacetic acid[21] are both toxic and should be handled with appropriate care. Cobalt(III) acetate was prepared by ozonation of cobalt(II) acetate and converted to cobalt(III) trifluoroacetate by ligand exchange in mixtures of trifluoroacetic acid and trifluoroacetic anhydride.[12,22] Reactions using acetaldehyde/oxygen as oxidant were performed in a Parr Model 4740 Hastelloy C high-pressure bomb. Product yields were determined by gas chromatography; analyses were performed on a Varian 3700 gas chromatograph using a 6-m 15% Apiezon L on Chromosorb W column, and mass spectral analyses were performed on a Finnigan 4000 GC/MS using a 30-m Durabond-1 medium-bore capillary column.

Trifluoroperacetic Acid as Oxidant. To a solution of benzene (0.428 g, 5.49 mmol) and cobalt(II) acetate (0.179 g, 1.01 mmol) in 50 mL of trifluoroacetic acid/10% trifluoroacetic anhydride at 25 °C was added 10 mL of a 0.5 M solution of trifluoroperacetic acid in trifluoroacetic acid/10% trifluoroacetic anhydride (cooled to 0 °C) by syringe pump over 20 h with stirring. The reaction mixture was initially a reddish pink that turned to dark green-black upon addition of the peracid. After the addition was complete, the reaction mixture was stirred an additional 7 h; completion of the reaction was indicated by the reddish brown color of the reaction mixture. Testing a sample of this reaction mixture with potassium iodide–starch test paper (Fisher) indicated that all the trifluoroperacetic acid had been consumed. The solution was then directly analyzed by gas chromatography using *n*-octane as an internal standard. The yield of phenyl trifluoroacetate was 56%, with a 58% conversion of benzene (selectivity to phenyl trifluoroacetate 96%). Oxidant selectivity (70%) was calculated from the yield of phenyl trifluoroacetate and the amount of oxidant consumed. Addition of water to the reaction mixture resulted in the quantitative conversion of phenyl trifluoroacetate to phenol and trifluoroacetic acid solvent.

The experiment above was repeated without the addition of cobalt(II) acetate to the reaction mixture, and only a 4.6% yield of phenyl trifluoroacetate was obtained.[23]

Peracetic Acid as Oxidant. A solution of benzene (0.043 g, 0.548 mmol) and cobalt(II) acetate (0.0187 g, 0.106 mmol) in 5 mL of trifluoroacetic acid/10% trifluoroacetic anhydride was stirred at 25 °C, and 0.010 mL of 35% peracetic acid (0.052 mmol) and 0.017 mL (0.12 mmol) of trifluoroacetic anhydride were added every 30 min for 10 h. An additional 0.042 g (0.54 mmol) of benzene was added to the solution, and eight more additions of peracetic acid and trifluoroacetic acid anhydride were added before the reaction was analyzed by gas chromatography using *n*-octane as internal standard. The yield of phenyl trifluoroacetate was 58%, with a 65% conversion of benzene (selectivity 89%).

Hydrogen Peroxide (30%) as Oxidant. To a solution of cobalt(II) acetate (0.177 g, 1.00 mmol) and benzene (0.0401 g, 0.51 mmol) in 5.0 mL of trifluoroacetic acid/20% trifluoroacetic anhydride at 0 °C was added 0.051 mL (0.50 mmol) of 30% hydrogen peroxide, and the solution stirred at 25 °C for 18 h. The resulting solution was analyzed by gas chromatography using *n*-octane as internal standard. The yield of phenyl trifluoroacetate was 12%, with a 20% conversion of benzene (selectivity 60%).

Acetaldehyde/Oxygen as Oxidant. Into a Parr bomb equipped with glass liner and Teflon-coated magnetic stirring bar were placed cobalt(II) acetate (0.0418 g, 0.236 mmol), benzene (0.0763 g, 0.98 mmol), acetaldehyde (0.044 g, 1.00 mmol), and 10 mL of trifluoroacetic acid. The bomb was pressurized to 1000 psi with oxygen and heated to 60 °C with stirring for 16 h. The yield of phenyl trifluoroacetate was 22%, with a 63% conversion of benzene (selectivity 35%).

Registry No. C_6H_6, 71-43-2; C_6H_5OH, 108-95-2; $(CF_3CO_2)_3CO$, 50517-80-1; $C_6H_5O_2CF_3$, 500-73-2.

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[23] Trifluoroperacetic acid or trifluoroperacetic acid–boron trifluoride reacts only slowly with benzene in the absence of a transition-metal catalyst to produce trace amounts of phenol: (a) Chambers, R. D.; Goggin, P.; Musgrave, W. K. R. *J. Chem. Soc.* **1959**, 1804–1807. (b) Hart, H.; Buehler, C. A. *J. Org. Chem.* **1964**, *29*, 2397–2400.

Propionyl and *n*-Butyryl Hypobromites and Hypoiodites as Intermediates in the Mercuric Propionate and *n*-Butyrate Induced Halogenation of Alkylbenzenes

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In studying the kinetics of the electrophilic attack of acetyl hypobromite and hypoiodite on aromatic hydrocarbons in acetic acid the use of solutions of mercuric acetate and bromine or iodine as the source of the highly reactive[1] acyl hypophalites has proved convenient.[2,3] In such solutions equilibria of the type shown in eq 1 are established. Equilibrium constants for the reactions (eq 2) can readily be obtained by a spectrophotometric method.

$$\mathrm{Hg(OC({=}O)R)_2 + X_2 \rightleftarrows Hg(OC({=}O)R)X + RCOOX} \tag{1}$$

$$K_{\mathrm{RCOOX}} = [\mathrm{Hg(OCOR)X}][\mathrm{RCOOX}]/[\mathrm{Hg(OCOR)_2}][\mathrm{X_2}] \tag{2}$$

The consumption of halogen by aromatic substances in such mixtures can also be followed by a spectrophotometric method. The equilibrium constants are then used to calculate [RCOOX] values from halogen concentrations during the course of the runs, and rate constants k are evaluated on the assumption that reaction proceeds according to the rate law in eq 3, where $[X_2]_T$ is the sum of the concentrations of free halogen and acyl hypohalite in the reaction mixtures.

$$d[\mathrm{ArX}]/dt = -d[\mathrm{X_2}]_\mathrm{T}/dt = k[\mathrm{ArH}][\mathrm{RCOOX}] \tag{3}$$

The equilibrium constant for the reaction of mercuric acetate and iodine in acetic acid is somewhat higher than

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the corresponding one for mercuric acetate and bromine, which probably reflects the relative resistance of bromine as compared to iodine to positive polarization occurring in the formation of acetyl hypohalite. Acetyl hypobromite is, however, a much more powerful halogenating agent than acetyl hypoiodite.

Mercuric trifluoroacetate reacts according to eq 1 with bromine in trifluoroacetic acid, but the equilibrium constant, K_{CF_3COOBr}, is very small, an indication of the strong resistance of bromine to highly positive polarization by the trifluoromethyl group of CF_3COOBr.[4] The hypohalite is, however, an *extremely* powerful halogenating agent. The equilibrium constant for formation of trifluoroacetyl hypoiodite in trifluoroacetic acid (eq 1) is considerably larger than that for the corresponding hypobromite. The hypoiodite is much less reactive in aromatic halogenation than trifluoroacetyl hypobromite.[5]

The shift from acetyl to trifluoroacetyl systems constitutes an extreme one in terms of the influence on hypohalite–aromatic hydrocarbon reactivity. A further investigation has been undertaken to assess the quantitative impact of less radical structural changes in acyl groups on acyl hypobromite and hypoiodite formation constants (eq 2) and reactivities in aromatic halogenation (eq 3). In the present report results are presented of a study of the reactions of bromine or iodine with mercuric propionate in propionic and with mercuric *n*-butyrate in *n*-butyric acid.

Experimental Section

Materials. Commercial samples of bromine (Mallinckrodt Analytical Reagent) and resublimed iodine (Baker and Adamson Reagent grade) were used without further purification. Mercuric propionate, mp 114–115 °C, and mercuric *n*-butyrate, mp 100–102 °C, were prepared by dissolving mercuric oxide (Mallinckrodt Analytical Reagent) in hot propionic and *n*-butyric acids, respectively, according to the procedure of Mukaiyama, Nambu, and Kuwajima.[6]

Propionic acid (Mallinckrodt analytical reagent) and *n*-butyric acid (Eastman Kodak) were treated with mercuric oxide and bromine to reduce trace impurities which consume halogen. In a typical procedure 15 g of the oxide were added gradually to 700 mL of the hot acid. The resultant cloudy solution was cooled, treated with 0.5 mL of bromine, allowed to stand at room temperature for 1 h, and distilled. Initial portions of the distillate gave a positive test for halogen. The remainder of the distillate, which became somewhat cloudy on standing, was redistilled. All but the last portion of the distillate tested negatively for halogen and was reserved for use in the equilibrium and rate measurements. Propionic acid was collected at bp 142 °C and the *n*-butyric acid from 160–162 °C.

Pentamethylbenzene (Eastman Organic Chemicals) was recrystallized twice from ethanol before use. A sample of Eastman Organic Chemicals toluene which had been distilled from *p*-toluenesulfonic acid was provided by Dr. Sevgi Friedrich. A sample of Mallinckrodt Analytical Reagent benzene was used without further purification.

Determination of the Equilibrium Constants for Formation of Propionyl and *n*-Butyryl Hypobromites and Hypoiodites. The spectrophotometric procedures for conducting the equilibrium studies were essentially the same as those employed in the determination of equilibrium constants, K_{CH_3COOX} (eq 2), for reaction of mercuric acetate with bromine and iodine in acetic acid.[2,3] The absorption maxima and molar absorptivities of bromine in propionic and *n*-butyric acid, as determined by measurements on solutions of the pure halogen, are 400 nm (186) in both acids and those for iodine in propionic and *n*-butyric acid are 480 (776) and 480 nm (770), respectively. In determining equilibrium constants (eq 2) certain solutions of very low bromine and iodine concentrations were avoided, as such solutions tended to undergo slow drops in halogen concentration (in the presence of mercuric propionate or *n*-butyrate), presumably due to reaction of trace impurities in the solvents with acyl hypohalites. As required, if eq 1 correctly accounts for the reaction of halogen with $Hg(OC({=}O)R)_2$, it has been shown by titration with standard sodium thiosulfate solution[2] that the oxidizing power of a solution of iodine in propionic acid is not changed by adding a solution of mercuric propionate, even though the amount of free iodine is reduced.

Table I. Equilibrium Constants for Formation of Propionyl Hypobromite and Hypoiodite in Propionic Acid and of *n*-Butyryl Hypobromite and Hypoiodite in *n*-Butyric Acid (25.0 °C)[a]

$10^3[Hg(OCOR)_2]_i$, M	$10^3[X_2]_i$, M	$10^3[X_2]_{eq}$, M	K_{RCOOX}
	Propionyl Hypobromite[b]		
96.2	14.4	5.03	0.202
48.1	8.67	3.48	0.180
19.2	4.33	1.96	0.171
9.6	4.33	2.42	0.196
9.6	2.17	0.97	0.177
			0.185 ± 0.011[d]
	n-Butyryl Hypobromite[b]		
96.0	13.8	4.95	0.182
72.0	20.7	10.2	0.176
57.6	24.8	14.5	0.155
48.0	8.28	2.84	0.245
			0.190 ± 0.028[d]
	Propionyl Hypoiodite[c]		
119.5	122	58.8	1.13
95.6	52.3	18.5	1.00
47.8	17.5	4.30	1.17
9.57	8.75	4.01	1.16
4.77	8.75	5.70	0.95
			1.07 ± 0.09[e]
	n-Butyryl Hypoiodite[c]		
40.3	36.0	16.3	1.16
40.3	18.0	4.95	1.27
20.2	18.0	8.20	1.13
10.1	18.0	11.4	1.09
10.1	9.00	3.78	1.47
			1.22 ± 0.12[d]

[a] The subscripts *i* in the column headings refer to initial concentrations; the subscript eq refers to free halogen concentrations at equilibrium. [b] $[X_2]$ is $[Br_2]$. [c] $[X_2]$ is $[I_2]$. [d] Average value. [e] Average of nine determinations.

The Bromination and Iodination Rate Studies. The procedures for investigating the rates of aromatic halogenation were analogous to those used in the earlier investigations.[2,3]

In the rate work it was necessary to keep the iodine and mercuric salt concentrations relatively low in order to avoid slow clouding of the rate samples (which interfered with the spectrophotometric measurements). Initial iodine concentrations did not exceed 3.5×10^{-3} M. The results of an investigation of limited scope indicated that the cloudy material was probably $Hg(OCOR)I$. The matter has not been further pursued.

Results and Discussion

Equilibrium constants, K_{RCOOX} (eq. 2), for formation of propionyl and *n*-butyryl hypobromites and hypoiodites at 25.0 °C are summarized in Table I. The constants for formation of the hypobromites, 0.185 for the propionyl and 0.190 for the *n*-butyryl, are approximately the same as that for acetyl hypobromite[2] (0.198) and much greater than that for trifluoroacetyl hypobromite[4] (2×10^{-4}). The constant for acetyl hypoiodite formation[3] (2.43) is about twice that for the propionyl (1.07) and *n*-butyryl (1.22) hypoiodites,

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(4) Barnett, J. R.; Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 6129.

(5) As reflected in σ^+ values of aromatic ring substituents; see: Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; p 356.

(6) Mukaiyama, T.; Nambu, H.; Kuwajima, I. *J. Org. Chem.* **1963**, *28*, 917.

Table II. Rate Constants for Toluene (Tol) Bromination and for Pentamethylbenzene (PMB) Iodination at 25.0 °C

$10^3[Hg(OCOR)_2]_i$, M	$10^3[Br_2]_i$, M	$[Tol]_i$, M	10^3k, M^{-1} s^{-1}
	Propionic Acid Solvent		
48.1	9.60	0.309	20
12.0	4.80	0.309	14
24.0	4.80	0.154	15
48.1	9.60	0.155	21
48.1	9.60	0.0772	24
	Butyric Acid Solvent		
35.4	9.75	0.467	7.3
70.7	9.75	0.233	9.9
56.6	15.6	0.187	9.6

$10^3[Hg(OCOR)_2]_i$, M	$10^3[I_2]_i$, M	$[PMB]_i$, M	10^3k M^{-1} s^{-1}
	Propionic Acid Solvent		
1.26	1.10	0.0866	5.1
2.52	1.10	0.0578	5.4
2.10	1.83	0.0481	6.2
3.16	3.26	0.0490	4.7
	Butyric Acid Solvent		
12.1	1.05	0.0972	1.6
20.1	1.80	0.0540	1.5
10.1	1.80	0.0540	1.2

and all three constants are substantially greater than that for trifluoroacetyl hypoiodite[4] (0.111). All the values for K_{RCOOX} for the hypoiodites are significantly larger than those for the corresponding hypobromites, in reflection of the relative ease of positive polarization of bromine and iodine.

The rate constants (eq 3) for bromination of toluene in solutions of mercuric propionate and bromine in propionic acid and mercuric n-butyrate and bromine in n-butyric acid and the corresponding ones for iodination of pentamethylbenzene are given in Table II. Though benzene reacts with acetyl hypobromite (in mixtures of bromine and mercuric acetate) in acetic acid at 25.0 °C at a rate suitable for spectrophotometric investigation, the reaction of propionyl hypobromite and benzene in propionic acid at 25.0 °C is too slow for convenient kinetic study. One rate run on the propionyl hypobromite–benzene reaction was allowed to proceed at room temperature (about 22 °C) long enough to follow its progress to better than 50% completion. From the results a rough value of $k = 6 \times 10^{-5}$ M^{-1} s^{-1} for the reaction of benzene and propionyl hypobromite was obtained.

In Table III a summary of the rate constants is provided and the constants are compared with those reported in earlier work.[2,3] As observed previously for the reactions of the acetyl hypohalites the propionyl and n-butyryl hypobromites are considerably more reactive than the hypoiodites. The three hypobromites are reactive enough that they are consumed at easily measurable rates at room temperature by either benzene or toluene, hydrocarbons which are not highly susceptible to electrophilic halogenation.[7] The much more reactive hydrocarbon, pentamethylbenzene, reacts with all three hypoiodites at rates generally comparable to those for reactions of the corresponding hypobromites with benzene or toluene. Clearly the difference in electrophilicity of the hypobromites and hypoiodites is substantial.

Table III. Relative Reactivities of Acyl Hypohalites with Aromatic Hydrocarbons[a]

Ar substrate	halogenating agent	solv	k (25.0 °C), M^{-1} s^{-1}	$k_{AcOX}/k_{PrOX}/k_{BuOX}$
benzene	AcOBr[b]	AcOH	3.2×10^{-3}	~50/1.0/0
	PrOBr	PrOH	$\sim 6 \times 10^{-5}$	
toluene	AcOBr	AcOH	1.5[c]	172/2.2/1.0
	PrOBr	PrOH	19.0×10^{-3}	
	BuOBr	BuOH	8.7×10^{-3}	
pentamethylbenzene	AcOI	AcOH	78×10^{-3}	56/3.6/1.0
	PrOI	PrOH	5.1×10^{-3}	
	BuOI	BuOH	1.4×10^{-3}	

[a] The abbreviations Ac, Pr, and Bu represent $CH_3C{=}O$, $CH_3CH_2C{=}O$, and $CH_3CH_3CH_2C{=}O$, respectively. [b] From ref 2. [c] Based on the composition of products of reaction of known mixtures of benzene and toluene with AcOBr in HOAc (ref 2).

Both for the hypobromites and hypoiodites (RCOOX) the reactivities fall off as R is changed in the order $CH_3 > CH_3CH_2 > CH_3CH_2CH_2$. The difference in reactivity of the acetyl and propionyl hypohalites is much larger than that for propionyl and n-butyryl hypohalites. The differences in reactivity are probably to a considerable extent related to differences in medium effects of acetic, propionic, and n-butyric acids and largely the result of differences in medium dielectric constants. The dielectric constant of acetic acid is significantly larger than the constants for propionic and n-butyric acids, which are similar to each other.[9] Though the halogenation reactions may be subject to acid catalysis, the acidities of these acids are closely similar.[8] Decreases in reactivities of the hypohalites with changes in R groups may also to some degree be associated with the relative inductive effects of those groups.

Registry No. PMB, 700-12-9; $Hg[OC(O)CH_2CH_3]_2$, 26719-04-0; $Hg[OC(O)(CH_2)_2CH_3]_2$, 19348-32-4; Br_2, 7726-95-6; I_2, 7553-56-2; $CH_3CH_2C(O)OBr$, 82198-80-9; $CH_3(CH_2)_2C(O)OBr$, 100814-78-6; $CH_3CH_2(O)OI$, 100814-79-7; $CH_3(CH_2)_2C(O)OI$, 100814-80-0; PhMe, 108-88-3; benzene, 71-43-2.

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[7] Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 4549.

[8] The K_A value for acetic acid at 25 °C is reported as 1.856×10^{-5}, while the corresponding values for propionic and n-butyric acids aare of the order of 1.4×10^{-5} and 1.5×10^{-5}, respectively (from: "Beilsteins Handbuch der Organischen Chemie"; Springer-Verlag: Berlin, 1920; Vol. II, pp 101, 236, 267).

[9] The dielectric constants for the three acids are 6.4 (20 °C) for acetic acid, 3.19 (19 °C) for propionic acid, and 2.85 (20°C) for n-butyric acid (from: "International Critical Tables"; McGraw-Hill: New York, 1929; Vol. VI, pp 84–87).

Dynamic Structures of Zinc, Magnesium, and Aluminum Azaallylmetal Reagents

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Azaallylmetal reagents are important and versatile reactive intermediates. Synthetically they are equivalent to metal enolates. These reagents are useful in electrophilic asymmetric synthesis in which electrophiles react with chiral 1-azaallylmetal reagents that have a homochiral group on nitrogen.[2] While lithium has been the most common metal used in azaallylmetal reagents, less electropositive metals are receiving more attention in this and

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[1] Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.

[2] Bergbreiter, D. E.; Newcomb, M. In "Asymmetric Syntheses"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 9.

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